Gas sensor with multiple internal reference electrodes and sensing electrodes

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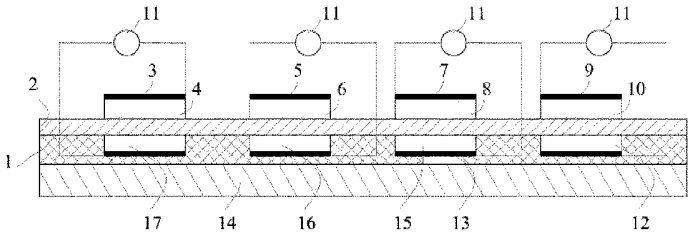


Fig. 3

(57) Abstract: The invention relates to a potentiometric gas sensor, or potentiometric gas detection element, with multiple internal reference electrodes and multiple sensing electrodes for determining the concentrations of gas components in a gaseous mixture. The sensor for gas detection comprises: a solid electrolyte, at least two sensing electrodes (SEs) in solid contact with the electrolyte, and at least two internal reference electrodes (IREs) in solid contact with the electrolyte, wherein each IRE comprises a composite material, comprising a binary mixture of a metal and a metal oxide dispersed to form a three-dimensional network extending throughout the IRE, and wherein each SE is electrically connected with at least one IRE.

Gas sensor with multiple internal reference electrodes and sensing electrodes

Field of invention

The invention relates to a potentiometric gas sensor, or potentiometric gas detection element, with multiple internal reference electrodes and multiple sensing electrodes for determining the concentrations of gas components in a gaseous mixture.

Background of invention

Detection of gas is important in a multiple of industrial applications, e.g. for monitoring and controlling combustion processes, welding and food storage. Gas sensors or gas detection elements are used for detection of gases, and the sensors are essential to improve combustion efficiency, reduce emissions and extend food shelf time. Gas sensors also play a key role for environmental compliance, e.g. for keeping environmental regulations on gasses such as nitrogen oxides (NO_x), carbon oxides (CO_x), hydrogen sulfide (H_2S), and sulfur oxides (SO_x).

A sensor for detection of oxygen was disclosed in WO 2013/160271 “Sensor employing internal reference electrode”. The oxygen sensor (denoted IROS) comprised an internal reference electrode (denoted IRE) and an oxygen sensing electrode (denoted SE). The benefits of the disclosed oxygen sensor were the avoidance of noble metals, reference gas supply, and an extension of the sensor operational temperature range towards lower temperatures.

However, a critical issue for the oxygen sensor disclosed in WO 2013/160271 is the lifetime of the IRE. The IRE comprises a binary mixture of metal/metal oxide that is depleted during operation. The depletion time is further described by some of the inventors in Solid State Ionics 240 (2013) 34-40. The reference teaches that the lifetime of the IRE can be increased by decreasing the operational temperature, or by increasing the sensor dimensions, such as the load of the binary components and thus the metal, or the electrolyte thickness. However, increasing the sensor dimensions (or the footprint) may be undesirable due to material costs and a less flexible use of the sensor.

Another critical issue for the sensor in WO 2013/160271 is that in case of failure, or at the end of lifetime of the IRE (i.e. at the critical metal depletion), the oxygen sensor has no back-up system. A method to recover the depleted components by electrochemical means is described. However during recovery the sensor would be non-operational, and a recovery period of 3 hours is described in WO 2013/160271. Thus, failure of the IRE as well as IRE recovery periods are critical issues for the industrial applicability of the described gas sensor.

The sensor disclosed in WO 2013/160271 is further restricted to the detection of a single gas specie, determined by the sensing electrode (SE), which as described in the application is suitable for oxygen detection.

Sensors with multi-gas functionality have previously been described. WO 97/42495 discloses a sensor comprising multiple electrodes, suitable for detection of multiple gases such as NO_x, CO_x, SO_x and O_2 (i.e. a sensor array). The sensor array may comprise multiple relative reference electrodes made of noble metals such as silver, gold, rhodium, platinum, and a reference electrode comprising a binary mixture such as Ni/NiO, Cu/CuO or the like.

The disclosed electrode geometries of WO 97/42495 show that each sensing electrode requires an individual relative reference electrode (i.e. the reference electrode is not shared). Thus, material costs and compactness of the sensor may be issues, and the material choices of the sensing electrodes and the electrolyte further suggest that high operational temperatures are required for the sensor to work.

WO 2009/049091 discloses a sensor array with multi-gas functionality. The sensor comprises multiple sensing electrodes and pseudo-reference electrodes, and the electrodes may be positioned coplanar (i.e. on the same side of the electrolyte) or on separate substrates, and be further integrated with a temperature control system. The temperature is based on surface temperature control. The use of pseudo-references of platinum is described and high operational temperatures above 400 °C is illustrated. Thus, the sensor array is believed restricted by the operational temperature range, reliability and costs.

Summary of invention

In this text, IRE is used as acronym for “internal reference electrode”, and IREs is used as acronym for multiple internal reference electrodes. Similarly, SE is used as acronym for “sensing electrode”, and SEs is used as acronym for multiple sensing electrodes.

Considering the prior art described above, an object of the present invention is to provide a sensor with an internal reference electrode (IRE) that can be operated continuously and with reduced risk of failure, and which further can be operated at low operational temperatures without the use of noble metals, and which optionally has multi-gas functionality and optionally compact dimensions and small footprint.

The object can be achieved by means of a sensor for gas sensing, comprising: a solid electrolyte, at least two sensing electrodes (SEs) in solid contact with the electrolyte, and at least two internal reference electrodes (IREs) in solid contact with the electrolyte, wherein each IRE comprises a composite material, comprising a binary mixture of a metal and a metal oxide dispersed to form a three-dimensional network extending throughout the IRE, and wherein each SE is electrically connected with at least one IRE.

The object can further be achieved by means of a method of fabricating a sensor, said method comprising the steps of: providing at least one electrolyte layer, at least two IREs, and one or more SEs, wherein the SEs and IREs are in solid contact with the electrolyte, and wherein the electrolyte separates the SE from the IRE, connecting the IREs and SEs, providing a power source, one or more switch(es), and connecting the power source and switch(es) to the IREs such that the IREs can be operated in three modes (working, idle, and recovery), and configured such that the operation of multiple IRE(s) can be controlled independently or dependently of each other. The object can be further achieved by optionally further providing electronic control means.

The introduction of multiple IREs makes it essential to control the temperature of each of the IREs, since the IRE operates by thermodynamic equilibrium principles. Another object of the present invention is therefore to provide a method of assembling a sensor with multiple IREs, with an integrated heating source and temperature control system.

The object can be achieved by means of a method of assembling a sensor with IREs with an integrated heating source and a temperature control system, said method comprising: providing one or more electrolyte(s), depositing onto the electrolyte(s) by screen-printing one or more ink(s) of an IRE, a heating element, a temperature detector, a conductive layer, and an insulation, wherein the order of the inks and the deposited pattern of the inks are configured to a defined design, and optionally laminating and co-sintering multiple screen-printed electrolytes.

A further object of the present invention is directed towards the use of a sensor with multiple IREs, which has multi-gas functionality and thus simultaneously can measure concentrations of O_2, and/or NO_x, and/or H_2S, and/or CO_x, and/or SO_x.

The object is obtained by the use of the sensor according to the invention for detection of oxygen, and/or NO_x, and/or CO_x, and/or H_2S, and/or SO_x.

Thus, the present invention makes it possible to improve the reliability and operational time of a sensor with internal reference electrodes (IREs). Furthermore, the present invention makes it possible to detect multiple gas species with a device which comprises IREs, and thus has the benefits of possible low operational temperature, avoiding expensive noble metals, simple installation, and a possible compact design as well as possibly flexible recovery options.

Most sensors comprising a solid electrolyte require a high operational temperature, for the electrodes to reach equilibrium sufficiently fast. A lower operational temperature, such as temperatures above only 300 °C, may be obtained by adding further materials to the electrodes. In an embodiment of the invention, each IRE comprises a further material or material mixture providing ion conductivity and electronic conductivity, and wherein the composite components, i.e. the binary mixture of a metal and a metal oxide, and the further material are dispersed to form a three-dimensional network extending throughout the IRE.

In a further embodiment of the invention, the solid electrolyte is an oxide ion conductor.

A sensor may be potentiometric or conductometric. In a further embodiment of the invention, the sensor is potentiometric.

To reduce the risk of simultaneous failure of the multiple IREs of the sensor, it may be an advantage that the sensor comprises IREs of different types. In a further embodiment of the invention, each of the IREs comprises different materials.

For easier fabrication steps, it may be advantageous that the sensor comprises IREs of the same type. In a further embodiment of the invention, all of the IREs comprise the same materials. In a further embodiment, the IREs are identical.

The risk of simultaneous failure of the IREs, may also be obtained by increasing the number of IREs. This may further be combined with the advantage of easy fabrication steps. Thus, in a further embodiment of the invention, the sensor comprises three or more IREs, and wherein the IREs optionally comprise the same materials.

During operation, or upon failure, the IRE becomes depleted, i.e. the ratio of the binary mixture of the IRE is changed as one of the components of the binary mixture of the IRE, in most of cases the metallic component is depleted. The ratio may be recovered by a current. Thus, in a further embodiment of the invention, the binary mixture of the IRE is configured such the ratio of the components in the binary mixture can be recovered by electrochemical means, i.e. the metallic component can be recovered.

To monitor the depletion of the IREs, and to control a recovery of an IRE, the sensor may be connected to an electronic control and/or monitor device. The operational mode of each IRE may further be controlled by switches. In a further embodiment of the invention, the sensor further comprises electronic control means, preferably a potentiostat, and one or more switches configured such that different operation modes of each IRE can be activated, such as working, idle, or recovery.

To ensure that a sensor always has a working IRE, it is advantageous that the switches can be controlled. In a further embodiment of the invention, the operation mode of each IRE is controlled independently of each other. In a further embodiment, the operational mode of each IRE is controlled dependently on each other. In an embodiment of the invention comprising at least three IREs, the switches are configured such that at least one IRE is in working mode, at least one IRE is in idle mode, and at least one IRE is in recovery mode. In a further embodiment of the invention comprising at least four IREs,

the switches are configured such that at least two IREs is in working mode, at least one IRE is in idle mode, and at least one IRE is in recovery mode.

The electronic control device may be compact. In a further embodiment of the invention, the switches are contained in one electronic device.

To ensure continuous operation, and increase operational stability, the SEs and IREs of the sensor may be connected in different ways. In an embodiment of the invention, each of the two or more SEs is electrically connected to a separate IRE. In a further embodiment, each of the two or more SEs is electrically connected to two or more IREs. In a further embodiment, each of the two or more SEs is electrically connected to the same two or more IREs.

The sensor may have multi-gas functionality, by comprising different types of SEs that are responding, or detecting, different types of gas species. In a further embodiment of the invention, the sensor comprises SEs configured for detecting different gas types, thereby obtaining multi-gas functionality. In a further embodiment, the SEs are configured for detection of oxygen, and/or NOx, and/or COx, and/or SOx, and/or H_2S.

To ensure continuous operation, and increase operational stability, for each gas type to be detected, the sensor may comprise multiple SEs of each type of SE. In a further embodiment of the invention, the sensor comprises at least two SEs for each gas type to be detected. In a further embodiment, the sensor comprises at least three SEs for each gas type to be detected, and wherein each SE is electrically connected to a separate IRE, and wherein each IRE is configured to be operated in the three modes (working, idle or recovery), and wherein the operation mode of each IRE can be configured to be controlled independently or dependently of each other.

As described earlier, it is essential to control the temperature of the sensor and the electrodes of the sensor. In an embodiment of the invention, the sensor further comprises an integrated heating source and a temperature control system, or parts of a temperature control system.

To increase the mechanical strength of the sensor, it may further comprise one or more substrate(s) or a support layer(s). In an embodiment of the invention, the sensor further comprises a substrate, or support layer.

To enable more accurate control of the temperature, and to make the sensor compact, the heating source and temperature control system, or parts of the heating source and temperature control system, may be integrated. In a further embodiment of the invention, the heating source and/or parts of the temperature control system, are embedded into the substrate, or support layer. In a further embodiment of the invention, the heating source and/or parts of the temperature control system are partially or completely covered by one or more insulating layer(s). In a further embodiment of the invention, one or more heating element(s) (such as a heater) and one or more temperature detector(s) are embedded into the substrate or support layer. In a further embodiment, a temperature detector is embedded into the substrate or support layer, and optionally partially or completely covered by one or more insulating layer(s).

Small sensors are advantageous for many applications, such as portable systems and other miniaturised applications. The sensor of the current application may be made more compact by decreasing the size of the electrodes. In a further embodiment of the invention, the contact area between each IRE and the solid electrolyte is below 9 mm^2, more preferably below 7 mm^2, and most preferably below 5 mm^2.

Apart from size flexibility, shape flexibility may also be advantageous for sensors in such applications. In a further embodiment of the invention, the sensor comprises two or more electrolytes. In a further embodiment, the IREs and SEs are disposed on opposite surfaces of the electrolyte. In a further embodiment, the IREs and SEs are disposed on the same surface of the electrolyte.

Description of Drawings

The invention will in the following be described in greater detail with reference to the accompanying drawings.

Fig. 1 shows a schematic cross-section of a sensor with one internal reference electrode (IRE) as disclosed in WO 2013/160271.

Fig. 2 shows the calculated life time (depletion period) as a function of the operational temperature and the oxygen partial pressure (pO_2) at the SE for an embodiment of a sensor comprising a binary mixture of Ni/NiO with a Ni load of 0.1 mmol·cm^2, and where the electrolyte thickness (L) is 200 µm, as disclosed in Q. Hu et al., Solid State Ionics 240 (2013) 34-40.

Fig. 3 shows an embodiment of the invention, where a sensor comprises four IREs (12,15,16,17) and four SEs (4,6,8,10), and where each SE is electrically connected to a separate IRE. The voltage of each connected pair of IRE and SE is monitored by four voltmeters (11). The IREs and SEs are disposed on opposite surfaces of an electrolyte (2), and all four IREs are sealed from the surroundings by a seal (1). The embodied sensor further comprises a conductive layer on each IRE (13), a conductive layer on each SE (3,5,7,9), and a substrate, or support layer (14).

Fig. 4 shows an embodiment of the invention, where a sensor comprises three IREs (12,15,16) and four SEs (4,6,8,10), and where two of the SEs (8,10) are electrically connected to separate IREs (12,15), and where two of the SEs (4,6) are electrically connected to the same IRE (16). The voltage of each connected pair of IRE and SE is monitored by four voltmeters (11). The IREs and SEs are disposed on opposite surfaces of an electrolyte (2), and all four IREs are sealed from the surroundings by a seal (1). The embodied sensor further comprises a conductive layer on each IRE (13), a conductive layer on each SE (3,5,7,9), and a substrate, or support layer (14).

Fig. 5 shows an embodiment of the invention, with a sensor, similarly to Fig. 3, comprising four IREs (12,15,16,17) and four SEs (4,6,8,10), and where each SE is electrically connected to a separate IRE. The voltage of each connected pair of IRE and SE is monitored by four voltmeters (11), and each pair of IRE and SE is further connected to a switch (21) configured such that each IRE can be set to three different operation modes: working (denoted W), idle (denoted I), and recovery (denoted R). The recovery mode is facilitated by a power source (22).

Fig. 6 shows an embodiment of the invention, with a sensor, similarly to Fig. 3, comprising four IREs (12,15,16,17) and four SEs (4,6,8,10), and where each SE is electrically connected to a separate IRE, and where the voltage of each connected pair of IRE and SE is monitored by four voltmeters (11). The embodied sensor further comprises a substrate (14), wherein elements for a heating source and for a temperature control system have been embedded for each IRE. Subjacent, or below, each IRE and embedded within the substrate are a heating element (18), and a temperature detection element (20). The heating element (18) (as well as the temperature detector (20), not shown) may be covered by one or two insulation layers (19).

Fig. 7 shows an embodiment of the invention, with a sensor with integrated heating source and temperature control system similar to Fig. 6. The potential of each connected pair of IRE and SE is monitored by four voltmeters (11), and each pair of IRE and SE is further connected to a switch (21) configured such that each IRE can be set to three different operation modes: working (denoted W), idle (denoted I), and recovery (denoted R). The recovery mode is facilitated by a power source (22). Two of the electrode pairs are in working mode (4,6), one is idle mode (8), and one is in recovery mode (10).

Fig. 8 shows an embodiment of the invention, where a sensor comprises two IREs (12,15) and two SEs (4,6), where each SE is electrically connected to a separate IRE, and where the IREs and SEs are disposed on the same surface of the electrolyte. The two IREs are sealed from the surrounding by two separate seals (1). The potential of each connected pair of IRE and SE is monitored by two voltmeters (11), and each pair of IRE and SE is further connected to a switch (21) configured such that each IRE can be set to three different operation modes: working (denoted W), idle (denoted I), and recovery (denoted R), and where the recovery mode is facilitated by a power source (22). The embodied sensor further comprises a conductive layer on each IRE (13), a conductive layer on each SE (3,5), and a substrate (14) with embedded heating elements (18) covered by two insulation layers (19), and temperature detection element (20) subjacent, or below, each IRE and each SE.

Fig. 9 shows a photograph of a sensor, where the white layer is electrolyte (2) of tape cast yttria stabilized zirconia (YSZ), and the four square-shapes are four individual

IREs (12,15,16,17) of screen-printed NiO/YSZ. The scale unit is mm. Four SEs (4,6,8,10) of $(La_{0.75}Sr_{0.25})_{0.95}MnO_3$/YSZ are placed on the opposite surface of the electrolyte, and not visible.

Fig. 10 shows measured voltages as a function of temperature for a sensor similar to the sensors shown in Fig. 9. "Pair 1, 2, 3 and 4" denotes each pair of electrically connected IRE and SE. "Theoretical" denotes the theoretical voltage based on the gas composition when the sensor is exposed to air in the temperature range from 350 to 650 °C.

Fig. 11 shows, in an exploded view, an embodiment of the inside structure of a sensor comprising integrated elements for a heating source and for a temperature control system. The sensor has two IREs (16, 17) and two SEs (4, 6). An electrolyte (12) separates the IREs (16, 17) from the SEs (4, 6), and the two SEs (4, 6) are made of different materials such that they are selectively responsive to oxygen and nitrogen oxides (NO_x). A heating element (18) and a temperature detector (20) are positioned between insulation layers (19), and substrates (14). The seal (1) isolates the two IREs (16, 17) from environment. Conductive layers (3, 5, 13) are used for further electronic connection of the IREs and SEs.

Detailed description of the invention

The present invention is directed to a gas sensor, and a potentiometric gas sensor, with multiple internal reference electrodes (IREs), methods of producing the sensor, and the use of the sensor.

The phrases "gas sensor" and "gas detection element" are used interchangeably herein, and refer to a device for measuring gas concentrations. The response of the sensor can be further processed to be e.g. displayed, transferred, stored or used for diagnosis. The gas detection elements of this invention is preferably potentiometric, which means that a voltage or a potential difference between two electrodes, such as an internal reference electrode (IRE) and a sensing electrode (SE), is used to detect the concentration of specific gas species.

A potentiometric gas sensor detects gas concentration based on a voltage generated between an electrode pair, of a reference electrode and a sensing electrode, where the electrode pair is separated by an electrolyte. The sensing electrode is in contact with the sample gas (i.e. the gas where the concentration is to be detected), and the reference electrode is fed with a reference gas of known concentration. For example, a potentiometric oxygen gas sensor detects the concentration of oxygen in the sample gas, and the reference gas is typically air. The supply of air to the reference electrode is a challenge, especially for applications in complicated industrial equipment or small portable devices.

An oxygen sensor with a single IRE was disclosed in WO 2013/160271, and Fig. 1 shows a schematic of the working principle disclosed in the application. The IRE comprises a binary mixture (M/MO_x) of a metal (M) and metal oxide (MO_x) that is sealed, such that the IRE reference potential is determined by the binary mixture at a given temperature. The resistance of the binary mixture varies with the mixture ratio between the composite components M/ MO_x. The voltage of the sensor is measured against a sensing electrode for oxygen (SE), which is exposed to the surroundings to be measured. A solid electrolyte separates the IRE and SE, and the voltage, measured between the metal leads, will express the oxygen partial pressure at the SE.

The sensor disclosed in WO 2013/160271 comprises an IRE wherein the binary mixture M/MO_x determines a reference oxygen partial pressure at a given temperature. However, one of the components of the binary mixture, in most of cases the metallic component, will be oxidised during operation (e.g. due to unavoidable electronic leak of the electrolyte), thereby depleting or exhausting the IRE of the metal. This will cause the voltage to approach zero and thus failure of the IRE.

It is demonstrated in WO 2013/160271 that the IRE can be recovered or “recharged”, by applying a voltage or “reversing the current”. Thus, using the same metal leads as shown in Fig. 1, when the current is reversed, the oxidised metal is reduced again to metal, while the SE acts as counter electrode. A recovery time of three hours was demonstrated. During the recovery time, the sensor operation as gas detector will be interrupted, i.e. it cannot be used.

The lifetime, or the period of metallic depletion, of an IRE depends on the sensor dimensions and the operational conditions. Fig. 2 shows the calculated life time (depletion period) as a function of the operational temperature, and the oxygen partial pressure (pO_2) at the SE for an embodiment of a sensor comprising a binary mixture of Ni/NiO with a Ni load of 0.1 mmol·cm^2, and where the electrolyte thickness (L) is 200 µm (cf. Q. Hu et al., Solid State Ionics 240 (2013) 34-40). It follows from the illustrated depletion rates that the depletion period can be several years, however in some cases e.g. at temperatures above 1000 °C it may be as short as a couple of hours. The reference further teaches that the lifetime can be increased by lower operational temperatures, lower pO_2 at the SE, higher initial metallic (M) load, and/or thicker electrolyte.

The current invention provides a sensor comprising a multiple of IREs, thereby providing a sensor that can be operated continuously and without interruptions, and which further have higher reliability, and optionally multi-gas functionality. Furthermore, the sensor of the invention has the potential of variable recovery periods (e.g. slow recovery), which may be needed and/or beneficial for some binary mixtures. In addition, the sensor of the invention has size flexibility, and thereby optionally a compact design.

Fig. 3 shows an embodiment of the invention, where a sensor comprises four IREs (12,15,16,17) and four SEs (4,6,8,10), and where each SE is electrically connected to a separate IRE. The voltage between of each connected pair of IRE and SE is monitored by four voltmeters (11), and the voltage of each voltmeter will then reflect the concentration of the gas specie that the respective SE is responsive to. The IREs and SEs are disposed on opposite surfaces of an electrolyte (2), and all four IREs are sealed from the surroundings by a seal (1). The embodied sensor further comprises a conductive layer on each IRE (13), a conductive layer on each SE (3,5,7,9), and a substrate, or support layer (14).

Each of the four IREs in Fig. 3 is sealed from the surrounding atmosphere. A hermetically gas tight seal that isolates the IRE from the surroundings is essential for the operation and for minimising depletion of the IRE. Suitable sealing materials may be ceramic materials as well as glasses, such as a mixture of alumina, silica and sodium oxide, or mixtures of other oxides such as alumina, silica, stabilised zirconia

(such as 3 mol % or 5 mol % yttria stabilized zirconia), and magnesium oxide. An examples of a glass composition is SiO_2 (68 wt %), Al_2O_3 (15 wt %) and Na_2O (17 wt %).

The materials of the seal (1), the electrolyte (2) and the substrate (14) can be the same materials or different. For example, they may all be made of yttria stabilized zirconia (YSZ). Similarly the conductive layers of IREs (13) and the conductive layers of SEs (3,5,7,9) can be of the same materials or different. For example, all the conductive layers (13,3,5,7,9) may be made of the noble metals such as platinum or gold, or made of a composite of platinum and YSZ. In the sensor facrication process, each seal (1), electrolyte (2) and substrate (14) may comprise multiple layers of ceramic tapes. It is also not necessary to place the conductive layers on the outside surface of the IRE and/or SE as illustrated in Fig. 3. The conductive layers may also be placed between the electrolyte (2) and the IREs and/or SEs.

The seal may be applied during the fabrication process of the sensor, using ceramic processing techniques known to the person skilled within the art, and may include techniques such as co-sintering (cf. Riegel et al., Solid State Ionics 152-153 (2002), 783).

Each SE in Fig. 3 is electrically connected to a separate IRE. The pair of a connected IRE and SE, may also be called corresponding electrodes, or electrode pair.

The electrical connectors may be metal leads (illustrated by the lines in Fig. 3). The leads may be prepared from any suitable electrically conducting material including noble metals such as gold, silver, platinum, other metals such as copper, nickel, steel, or any alloys thereof, or conductive oxides such as $La(NiFe)O_3$, $(LaSr)MnO_3$ and $(LaSr)(CrFe)O_3$.

The electrical connectors may be configured such that they are suitable for being connected to a mean for electronic control. The mean for electronic control may be capable of measuring potential or voltage, as well as applying, or inducing, a voltage across the cell. Examples of suitable means for electronic control are a potentiostat, galvanostat, and a power source.

In Fig. 3, to further facilitate the electronic connection between the electrodes, a conductive layer (13) may be deposited on the surface of the IREs. The conductive layer may be of platinum (Pt) or a composite of Pt and yttria stabilized zirconia (YSZ).

In Fig. 3, the four SEs (4,6,8,10) are disposed on the opposite surface of the electrolyte as the IREs. The electrolyte (2) must be dense and gastight and comprise an oxide ion conductive material, such as stabilized zirconia or doped ceria, thereby providing oxide ion conduction between the IRE and the SE, which result in the voltage between the IRE and SE.

In Fig. 3, the four SEs (4,6,8,10) are detecting a gas specie, by the SE responding to the gas specie. The four SEs may be responsive to the same gas, or responsive to different gasses, or selectively responsive to specific gas species. The different gases that the SEs may be responsive to, or selectively responsive to, include oxygen (O_2) carbon oxide species (e.g. CO_2), nitrogen oxide species (e.g. NO_x), hydrogen sulfide (H_2S) and sulphur oxide species (e.g. SO_x).

When the SEs (4,6,8,10) are responsive to different gasses, the sensor can simultaneously detect different gas species. The material of the SE will determine which gas species, the SE is detecting or responding to, or if the SE is selectively responsive to a gas specie. In Fig. 3, the first SE (4) may be responsive to oxygen, and consist of a composite of 8 mol % yttria stabilized zirconia (8YSZ) and $(La_{0.75}Sr_{0.25})_{0.95}MnO_{3\pm\delta}$, optionally with infiltrated nano-sized samaria doped ceria (SDC). The second SE (8) may be responsive to NO_x and comprise $Ba(NO_3)_2$ and $CaCO_3$ with a molar ratio of 9:1, the third SE (6) may be responsive to CO_2 and comprise $Sc_2(WO_4)_3$, and the fourth SE (10) may be responsive to SO_x and comprise of Ag_2SO_4 and $BaSO_4$ in equal molar ratio.

To further facilitate the electronic connection between the electrodes, a conductive layer (3,5,7,9) may be deposited on the surface of the SEs as illustrated in Fig. 3. The conductive layer may be of any metal, such as silver, gold or platinum, and/or comprise conductive oxides such as $LaNi_{0.6}Fe_{0.4}O_3$.

The conductive layers (3,5,7,9) of the SEs may inherently have additional advantageous functionalities, e.g. the conductive layer may further function as catalyst

for conversion of gas species. A conductive layer of platinum will for example catalyse the conversion of sulphur dioxide SO_2 to sulphur trioxide SO_3. This can have the advantage that a SE which is only responsive SO_3, can also detect the catalyst converted SO_2, and thus will detect the total content of sulphur oxides (SO_X).

The sensor embodied in Fig. 3 further comprises a substrate, or support, (14). The substrate may provide additional mechanical strength to the sensor. The material of the substrate can be alumina, stabilised zirconia, or the composite thereof. It is preferably stabilised zirconia, when the electrolyte (2) and the seal (1) is also stabilised zirconia. Thereby the thermal expansion coefficient of the substrate is similar to the electrolyte (2) and the seal (1), and the support is chemical compatible with the electrolyte and the seal.

The IREs in Fig. 3 are similar to the internal reference electrode disclosed in WO 2013/160271, and may comprise of a composite, comprising a binary mixture of Ni/NiO, finely dispersed 8YSZ particles and optionally further dispersed nano-sized SDC particles. The binary mixture of Ni/NiO may be fabricated from a precursor of NiO, by electrochemical reduction of the precursor NiO, such as under conditions of a voltage of 1.1 V for 1 hour at 664 °C.

The IREs as embodied in Fig. 3 may be comprised of the same materials, such as a composite mixture of Ni/NiO, 8YSZ and SDC. The IREs may furthermore be identical, i.e. comprising the same compositions and same mixture ratios. The IREs may also comprise of different materials and/or mixtures in different ratios.

A sensor such as the one embodied in Fig. 3 may be fabricated by conventional ceramic processing technologies known to the skilled person, and include methods such as tape casting, screen printing, lamination and co-sintering.

The number of IREs and SEs of a sensor may be the same, or may be different. The sensor embodied in Fig. 4 comprises three IREs (12,15,16) and four SEs (4,6,8,10). Two of the SEs (8,10) are electrically connected to separate IREs (12,15), and two of the SEs (4,6) are electrically connected to the same IRE (16). The voltage of each connected pair of IRE and SE is monitored by four voltmeters (11). The IREs and SEs are disposed on opposite surfaces of an electrolyte (2), and all four IREs are sealed

from the surroundings by a seal (1). The embodied sensor further comprises a conductive layer on each IRE (13), a conductive layer on each SE (3,5,7,9), and a substrate, or support layer (14).

The electrical connection between an IRE and a SE may further comprise a switch (21), as illustrated in Fig. 5. The switch is configured such that the IRE of an electrode pair (i.e. a pair of connected IRE and SE) can be set to three different operation modes: working mode (denoted W), idle mode (denoted I), and recovery mode (denoted R). Thus, the operation modes can be activated by the switches.

When the switch of an electrode pair is in working mode, the IRE and SE are connected via a voltmeter, which will read the cell voltage of the electrode pair, and the electrode pair will thus detect a gas concentration.

When the switch of an electrode pair is in recovery mode, the IRE and SE are connected via a power source (22), which can supply a current. If the IRE has become depleted (i.e. the binary mixture ratio of e.g. Ni/NiO has changed and become very low), the IRE can be recovered by an electrical current, which can increase the binary mixture ratio of Ni/NiO. As the resistance of IRE depends on the ratio of Ni to NiO, switching of modes can be triggered according to the resistance of the IRE.

When the switch of an electrode pair is in idle mode, the IRE and SE are disconnected, i.e. not electrically connected. Thus, in idle mode the IRE is inactive. The idle mode can be selected if an electrode pair is waiting to enter recovery mode.

Methods and technologies for realizing the mode changes including the switch, power source and voltmeter is well known a person skilled in the art, and can e.g. be integrated into one electronic device such as an electrochemical station.

Due to the different operation modes of the multiple IREs of the sensor, it is possible to obtain a sensor with continuous operation. The operation modes of the multiple electrode pairs may be controlled independently or dependently. When an IRE fails or is depleted, it can be switched to recovery mode, while the other IREs will continue to be in working mode. When an IRE fails or is depleted and is switched to recovery mode, an IRE in idle mode or recovery mode may be switched to be in working mode.

The switching between the three operation modes may be triggered by a change in the electrical resistance. An IRE close to failure or depletion will be characterised by a different resistance than a working IRE or a recovered IRE. The resistance may be measured by a resistance gauge.

The multiple IREs further facilitate flexible recovery procedures and -periods. Since the sensor is still operational by another IRE, when an IRE is depleted and set to recovery mode, it may not be needed to recover the depleted IRE as quickly as possible. For some IREs it may be essential or beneficial with slower recovery procedures, since the quickest recovery period may not be the one resulting in the longest lifetime of the recovered IRE.

In addition, the multiple IREs facilitate flexible IRE size. Since the sensor can be kept operational by a multiple of IREs, the lifetime of each IRE becomes less critical. Thus, IREs with shorter lifetime, such as IREs with smaller dimensions (e.g. thinner electrolyte, or lower initial metallic load, or smaller footprints) can be applied. The footprint is represented as the contact area between each IRE and the electrolyte.

To further increase the sensor's continuous operational reliability, the operational mode of each IRE may be controlled independently, or preferably dependently, by means known to a person skilled in the art.

For some application, e.g. for sensors detecting toxic gasses or monitoring critical processes, a lapse in the functioning of the sensor may be very critical. To further increase the reliability of continuous operation of the sensor, the sensor may comprise two electrode pairs in working, and two electrode pairs in idle and/or recovery.

The sensor of the current invention should be operated at elevated temperatures such as above 300 °C, and precise temperature control is needed for accurate detection of a gas concentration. Furthermore, for accurate and reliable sensor operation, it is essential that the electrodes can reach thermodynamic equilibrium during operation. Hence, the temperature of the entire sensor and each sensor electrode in particular, must be controlled. It is therefore advantageous to integrate a heating source and a temperature control system, or parts of a temperature control system, with the sensor.

Fig. 6 shows an embodiment of a sensor with integrated heating source (18), such as a heater or heating element, and temperature control system elements (20), such as temperature detector (20). The integrated heating source an temperature control elements are integrated or embedded into the substrate (14) immediately subjacent or below the IREs and SEs. The heater (18) and the temperature detector (20) may be covered by one or two insulation layers, partially or completely (19).

The heating element may be a resistive heating element, and the temperature control system element, may be a temperature detector, such as a resistance temperature detector (RTD), where the resistance is detected to evaluate the temperature. The RTD may be made of platinum or a platinum/YSZ composite, which may be screen-printed. Insulation layers (19) may be disposed to cover the heating element (18), in case of large current passing through the heating elements, which may be detrimental and cause noise to the measured results. The material of the insulation layer can be alumina or the composite of alumina and YSZ.

Fabrication of a sensor with integrated heating elements and temperature detector may include the use of methods such as tape casting, screen printing, lamination and co-sintering, which is known to the skilled person (see Riegel, et al., (2002) Solid State Ionics 152-153: 783).

A sensor comprising integrated temperature elements and temperature detectors, and electrode pairs in different operation modes is shown in Fig. 7.

The IREs and SEs may also be disposed on the same surface of the electrolyte as illustrated in Fig. 8. The two IREs of Fig. 8 are then sealed from the surrounding by two separate seals (1).

Figs. 9 shows a photograph ofa fabricated sensor. The white layer is an electrolyte (2) of tape cast YSZ, and the four square-shapes are four individual IREs (12,15,16,17) of screen-printed NiO/YSZ. Four SEs (4,6,8,10) of $(La_{0.75}Sr_{0.25})_{0.95}MnO_3$/YSZ are placed on the opposite surface of the electrolyte, and not visible.

A sensor as shown in Fig. 9 was tested and the results are shown in Fig. 10, showing voltage measurements as a function of temperature. “Pair 1, 2, 3 and 4” denotes each pair of electrically connected IRE and SE. “Theoretical” denotes the theoretical potential based on the gas composition the sensor is exposed to air in the temperature range from 350 to 650 °C.

Fig. 11 shows, in exploded view, another embodiment of the inside structure of a sensor comprising integrated elements for a heating source and for a temperature control system. The sensor has two IREs (16, 17) and two SEs (4, 6). An electrolyte (12) separates the IREs (16, 17) from the SEs (4, 6), and the two SEs (4, 6) are made of different materials such that they are selectively responsive to oxygen and nitrogen oxides (NO_x). A heating element (18) and a temperature detector (20) are positioned between insulation layers (19), and substrates (14). The seal (1) isolates the two IREs (16, 17) from the environment. Conductive layers (3, 5, 13) are used for further electronic connection of the IREs and SEs.

Internal reference electrodes (IREs)

The preferred types of the IREs in the current invention is similar to the IRE disclosed in WO 2013/160271. However, each IRE of a sensor with multiple IREs may comprise different materials and/or different microstructures. The IREs of a sensor with multiple IREs may also comprise the same materials and microstructures, or optionally the IREs may be identical both in materials and microstructure.

The IRE is a composite material. By the term composite as used herein is meant a material made from two or more constituent materials, or material components. Within each IREs, the composite components are dispersed to form a three-dimensional network extending throughout the entire structure of the electrode. The IRE comprises a binary mixture of a metal and a metal oxide.

The binary mixture metal/metal oxide is selected among nickel/nickel oxide, palladium/palladium oxide, iron/iron oxide, cobalt/cobalt oxide, copper/copper oxide, tungsten/tungsten oxide, titanium/titanium oxide, vanadium/vanadium oxide, chromium/chromium oxide, manganese/manganese oxide, zinc/zinc oxide, niobium/niobium oxide, molybdenum/molybdenum oxide, ruthenium/ruthenium oxide,

rhodium/rhodium oxide, silver/silver oxide, cadmium /cadmium oxide, indium/indium oxide, tin/tin oxide, antimony/antimony oxide, tellurium/tellurium oxide, tantalum/tantalum oxide, rhenium/rhenium oxide, osmium/osmium oxide, iridium/iridium oxide, platinum/platinum oxide, thallium/thallium oxide, lead/lead oxide, preferably among nickel and nickel oxide, cobalt and cobalt oxide, iron and iron oxide, palladium/palladium oxide, as well as rhodium and rhodium oxide.

In addition to the binary mixture metal/metal oxide, the IRE comprises a further material or material mixture, which provides ion and electron conductivity. The further material is also dispersed to form a three-dimensional network extending throughout the IRE, i.e. throughout the entire structure of the electrode.

The further material or material mixture providing ion and electron conductivity is selected among ceramic materials and refractory oxides. More specifically, the further material is selected among:

1) Undoped perovskites with general formula:
PMO_3 where P=La, Sr, and M=Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Al.

2) Layered oxides with undoped perovskite-like structures with general formula:
P_2MO_4 where P = La, Sr and M= Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Al.

3) A-site doped perovskites with general formula:
$(P_{1-x}Q_x)_yMO_3$ where P=La, Y, Pr, Tb, Q=Ca, Sr, Ba, and M= Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Al (with $0 \leq x \leq 1$ and $0 \leq y \leq 1$, preferably $0.25 \leq x \leq 0.55$ and $0.95 \leq y \leq 1$).

4) A- and B-site doped perovskites with general formula:
$(P_{1-x}Q_x)M_{1-y}N_yO_3$ where P = Y, Ca, Sr, Ba, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Q = Y, Ca, Sr, Ba, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu such that the elements chosen for P and Q are different from each other; M= Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Al and N= Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Al such that the elements chosen for M and N are different from each other, with $0 \leq x \leq 1$ and $0 \leq y \leq 1$, preferably $0.25 \leq x \leq 0.55$ and $0.25 \leq y \leq 0.55$;

5) Zirconia based solid solutions:
ZrO_2-MO where M=Mg, Ca.
ZrO_2-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.
ZrO_2-Bi_2O_3-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

6) Hafnia based solid solutions:

HfO_2-MO where M=Mg, Ca.

HfO_2-M_2O_3 where M= Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

7) Ceria based solid solutions:

CeO_2-MO where M=Mg, Ca, Sr.

CeO_2-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

8) Thoria based solid solutions:

ThO_2-MO where M=Mg, Ca, Sr, Ba.

ThO_2-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

9) Urania based solid solutions:

UO_2-MO where M=Mg, Ca, Sr, Ba.

UO_2-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

10) Bismuth oxide based solid solutions:

Bi_2O_3-MO where M=Mg, Ca, Sr, Ba, Pb.

Bi_2O_3-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb.

Bi_2O_3-WO_3.

$Bi_2O_3 \cdot (PbO)_{1-x} \cdot (CaO)_x$, with $0 \leq x \leq 1$, preferably $0.4 \leq x \leq 0.8$.

11) Oxygen saturated fluorites:

CaF_2-CaO.

BaF_2-BaO.

and any mixtures thereof.

Preferred materials are zirconia based solid solutions and ceria based solid solutions, more preferably yttria stabilised zirconia (ZrO_2-Y_2O_3, also known as YSZ), gadolinia doped ceria (CeO_2-Gd_2O_3, also known as GDC), and samaria doped ceria (CeO_2-Sm_2O_3, also known as SDC), and mixtures thereof.

The particle sizes of the binary mixture metal/metal oxide and/or the particles of the further material or material mixture providing ion conductivity and electron conductivity lies in the range of less than 200 µm, and more preferably in the range of less than 100 nm.

The IREs may be fabricated by conventional wet ceramic techniques, such as powder mixing, and printing or tape casting of slurries of the material mixtures. The methods are known from fields such as ceramic materials, fuel cells and electrolysis cells. Additional fabrication techniques may be combined with the conventional techniques,

such as metal reduction, either chemically or electrochemically (i.e. by externally applied voltage), and impregnation (also known as ion impregnation or infiltration). The additional techniques are also known from the fields of fuel cells and electrolysis cells.

A preferred IRE fabrication method comprises: mixing the further material (or the material mixture providing ion and electron conductivity) with the metal oxide of the binary mixture metal/metal oxide, formation of the principle IRE structure, and as the final step the metal of the binary mixture metal/metal oxide is prepared by electrochemical reduction of the metal oxide.

Another preferred IRE fabrication method comprises adding and dispersing the further material into the formed binary mixture metal/metal oxide by impregnation. The method is known to introduce finely dispersed nanoparticles in the range of less than 100 nm, and preferably less than 50 nm.

Sensing electrodes (SEs)

The material of a SE should be selectively responsive to the gas species to be detected, and the response is further required to be reflected in the cell voltage between the SE and the corresponding IRE (i.e. the IRE electrically connected to the SE).

Suitable SE materials fulfilling the requirements for detection of different gas species have been demonstrated, such as SE materials for oxygen detection, and detection of NO_x, CO_x, SO_x, and H_2S. The SE materials may be in combination with any solid electrolyte, such as an electrolyte of yttria-stabilised zirconia or magnesia-stabilised zirconia.

By the term "NO_x" as used herein is meant nitrogen oxide species such as N_2O, NO, N_2O_3, NO_2, N_2O_4, N_2O_5 and mixtures of these, preferably NO, NO_2 and mixtures of NO and NO_2. Nitrogen oxides may also be denoted as "nitro oxides".

By the term "SO_x" as used herein is meant sulphur oxide species such as SO, S_2O_3, SO_2, SO_3, S_2O_7, SO_4 and mixtures of these, preferably SO_2, SO_3, and mixtures of SO_2 and SO_3.

By the term "CO_x" as used herein is meant carbon oxide species such as C_3O_2, CO, and CO_2, and mixtures of these, preferably CO, CO_2, and mixtures of CO and CO_2.

The sensor of the current invention comprises multiple SEs. The multiple SEs may either be of the same type (e.g. only SEs for oxygen detection), or of different types, such as a SE for oxygen detection and a SE for NO_x detection. When the sensor comprise different types of SEs, it is possible to simultaneously monitor different species in a multi-component gas. The sensor may also comprise a mixture of multiple SEs of the same types and of different types, such as multiple SEs for oxygen detection, and/or multiple SEs for NO_x detection, and/or multiple SEs for CO_x detection, and/or multiple SEs for SO_x detection, and/or multiple SEs for H_2S detection.

Each pair of electrodes (i.e. electrically connected IRE and SE) may further comprise a switch configured to be operated in the three modes (working, idle and recovery).

Materials for a SE selectively responsive to NOx gasses are known to the skilled person. These include materials comprising: $(La_{0.8}Sr_{0.2})(Co_{0.9}Ru_{0.1})O_3$, and mixtures of La_2CuO_4 and $(La_{0.8}Sr_{0.2})(Co_{0.9}Ru_{0.1})O_3$, $Ba(NO_3)_2$ and mixtures of $Ba(NO_3)_2$-$CaCO_3$, $Sr(NO_3)_2$, KNO_3, $CsNO_3$, mixtures of $Ba(NO_3)_2$–$BaCO_3$, mixtures of $NaNO_3$-$Ba(NO_3)_2$, mixtures of $NaNO_2$-Li_2CO_3, mixtures of $NaNO_3$-Li_2CO_3, and mixtures thereof.

Materials for a SE selectively responsive to COx gasses are known to the skilled person. These include materials comprising: SnO_2, ZnO, In_2O_3 and mixtures thereof, optionally containing other metals or metal oxides to enhance the CO selectivity further, which may be Rb_2O, Au-La_2O_3, and ThO_2. The materials may also comprise $Sc_2(WO_4)_3$, Li_2CO_3, K_2CO_3, Na_2CO_3, $La_2(CO_3)_3$, $La_2(WO_4)_3$, mixtures of $Sc_2(WO_4)_3$-Li_2CO_3, mixtures of $La_2(WO_4)_3$-Li_2CO_3, $CaCO_3$, $SrCO_3$, $BaCO_3$, SnO_2, ZnO, In_2O_3, and mixtures thereof.

Materials for a SE selectively responsive to SOx gasses are known to the skilled person. These include materials comprising: Li_2SO_4, $BaSO_4$, Ag_2SO_4, WO_3, MgO, mixtures of Li_2SO_4-$CaSO_4$-SiO_2 (such as in 4:4:2 in molar ratio), mixtures of Li_2SO_4-MgO (such as in 8:2 in molar ratio), and mixtures of Ag_2SO_4-$BaSO_4$ (such as in 1:1 in molar ratio).

Materials for a SE selectively responsive to H_2S gasses are known to the skilled person. These include materials comprising: WO_3.

The preferred type of SEs for oxygen detection in the current invention is of the same type as the SE disclosed in WO 2013/160271. The SE for oxygen detection is a composite, comprising a material or material mixture providing ion conductivity, and a material or material mixture providing electron conductivity.

The oxygen SE composite components are dispersed to form a three-dimensional network extending throughout the entire SE structure, such that the particles of the material providing ion conductivity, and the particles of the material providing electron conductivity, are finely dispersed within the entire SE.

The size of the particles of the material providing ion conductivity and/or the particles of the material providing electron conductivity, lies in the range of less than 200 µm, and more preferably in the range less than 100 nm.

The oxygen SEs may be fabricated by conventional wet ceramic techniques, such as powder mixing, and printing or tape casting of slurries of the material mixtures, and impregnation. The methods are known from fields such as ceramic materials, fuel cells and electrolysis cells. A preferred method include the mixing of all particles from the beginning of the preparation, e.g. by ball-milling, then followed by shaping, e.g. by printing, and consolidating the structure by sintering. Another preferred method includes the mixing of some of the particles, shaping and sintering them, and then add additional particles by ion impregnation.

Both the material providing ion conductivity within the oxygen SE, as well the material providing electron conductivity within the oxygen SE, is selected among ceramic materials and refractory oxides.

More specifically, the materials providing respectively ion conductivity and electron conductivity are selected among:

1) Undoped perovskites with general formula:

PMO_3 where P=La, Sr, and M=Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Al.

2) Layered oxides with undoped perovskite-like structures with general formula:

P_2MO_4 where P = La, Sr and M= Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Al.

3) A-site doped perovskites with general formula:

$(P_{1-x}Q_x)_yMO_3$ where P=La, Y, Pr, Tb, Q=Ca, Sr, Ba, and M= Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Al (with $0 \leq x \leq 1$ and $0 \leq y \leq 1$, preferably $0.25 \leq x \leq 0.55$ and $0.95 \leq y \leq 1$).

4) A- and B-site doped perovskites with general formula:

$(P_{1-x}Q_x)M_{1-y}N_yO_3$ where P = Y, Ca, Sr, Ba, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Q = Y, Ca, Sr, Ba, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu such that the elements chosen for P and Q are different from each other; M= Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Al and N= Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Al such that the elements chosen for M and N are different from each other, with $0 \leq x \leq 1$ and $0 \leq y \leq 1$, preferably $0.25 \leq x \leq 0.55$ and $0.25 \leq y \leq 0.55$;

5) Zirconia based solid solutions:

ZrO_2-MO where M=Mg, Ca.

ZrO_2-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

ZrO_2-Bi_2O_3-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

6) Hafnia based solid solutions:

HfO_2-MO where M=Mg, Ca.

HfO_2-M_2O_3 where M= Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

7) Ceria based solid solutions:

CeO_2-MO where M=Mg, Ca, Sr.

CeO_2-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

8) Thoria based solid solutions:

ThO_2-MO where M=Mg, Ca, Sr, Ba.

ThO_2-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

9) Urania based solid solutions:

UO_2-MO where M=Mg, Ca, Sr, Ba.

UO_2-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

10) Bismuth oxide based solid solutions:

Bi_2O_3-MO where M=Mg, Ca, Sr, Ba, Pb.

Bi_2O_3-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb.

Bi_2O_3-WO_3.

$Bi_2O_3 \cdot (PbO)_{1-x} \cdot (CaO)_x$, with $0 \leq x \leq 1$, preferably $0.4 \leq x \leq 0.8$.

11) Oxygen saturated fluorites:

CaF_2-CaO.

BaF_2-BaO
and any mixtures thereof,
preferably wherein the material providing electron conductivity is selected among optionally doped $LaMnO_3$, $LaCoO_3$, (La,Sr)MnO_3, ZrO_2, and CeO_2, more preferably yttria stabilized zirconia and lanthanides based oxides, wherein the lanthanides preferably are selected among Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

Most preferably, the composite SE comprises (La,Sr) MnO_3 (LSM), ZrO_2-Y_2O_3 (YSZ) and CeO_2-Sm_2O_3 (SDC).

Electrolyte

The electrolyte must be dense and gastight, and provide oxide ion conduction between the IRE and the SE, which facilitates the establishment of the thermodynamic equilibrium of the IRE and SE.

The thickness of the electrolyte is a factor on the expected IRE lifetime. A preferred thickness is in the range of 300 µm, and more preferably in the range of 200 µm.

The electrolyte may be fabricated by conventional wet ceramic techniques, including powder mixing, and printing or tape casting of slurries of the material mixtures. The methods are known from fields such as ceramic materials, fuel cells and electrolysis cells.

The material providing oxide ion conductivity of the electrolyte is selected among:
1) Zirconia based solid solutions:
ZrO_2-MO where M=Mg, Ca, Ba.
ZrO_2-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.
ZrO_2-Bi_2O_3-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.
2) Hafnia based solid solutions:
HfO_2-MO where M=Mg, Ca, Sr, Ba.
HfO_2-M_2O_3 where M= Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.
3) Ceria based solid solutions:
CeO_2-MO where M=Mg, Ca, Sr, Ba.
CeO_2-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

4) Thoria based solid solutions:

ThO_2-MO where M=Mg, Ca, Sr, Ba.

ThO_2-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

5) Urania based solid solutions:

UO_2-MO where M=Mg, Ca, Sr, Ba.

UO_2-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

6) Bismuth oxide based solid solutions:

Bi_2O_3-MO where M=Mg, Ca, Sr, Ba, Pb.

Bi_2O_3-M_2O_3 where M=Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb.

Bi_2O3-WO_3.

$Bi_2O_3 \cdot (PbO)_{1-x} \cdot (CaO)_x$, with $0 \leq x \leq 1$, preferably $0.4 \leq x \leq 0.8$;

7) Oxygen saturated fluorites:

CaF_2-CaO.

BaF_2-BaO.

and any mixtures thereof.

Preferred materials are zirconia based solid solutions, more preferably 10 mol% Sc_2O_3 and 1 mol% Y_2O_3 stabilised zirconia (also known as ScYSZ).

Temperature control system

For accurate and reliable sensor operation, it is essential that the electrodes can reach thermodynamic equilibrium during operation. Hence, the temperature of the entire sensor and each sensor electrode in particular, must be controlled. It is therefore advantageous to integrate a heating source and a temperature control system, or parts or elements therof, with the sensor.

A temperature control system typically comprises temperature detectors, or thermocouples, and a heating source, which may be a heating element such as a resistive heater. The configuration, or relative positions, of the thermocouples and the heating source, or heating elements, determines the precision of the temperature control system.

The configuration of the heating source and the temperature control system may be as illustrated in Figs. 6, 7, and 8, where the elements are embedded into a substrate, such

that they are placed in the substrate below, or subjacent, each electrode (IRE and/or SE). Thus, in the substrate subjacent each electrode, is placed a heating element (18), optionally with insulation layers (19), and a temperature detection element.

Other configurations of the heating source and temperature control system elements may be possible. Any number of embedded elements may be embodied, such as one heating element. Furthermore, any dimension and position of the embedded elements may be embodied, such as a heating element embedded and extending through a larger part of the substrate, thus not only placed immediately subjacent to an electrode.

The embodied heaters, are resistive heating elements, and may be made of metals such as tungsten, platinum, molybdenum, or of electronic conducting oxides such as lanthanum strontium manganites. The resistive heating elements may be a composite made of metal and oxides such as platinum and yttria stabilized zirconia.

Examples

Example 1: Sensor with four IREs and four SEs

A sensor as illustrated in Fig. 9 comprising four IREs and four SEs, was prepared. The fabrication steps were:

Step 1: preparation of solvent.
PVP (Polyvinylpyrrolidone, K-15), PVB (polyvinyl butyral, B75H), PEG (Polyethylene glycol, PEG1000) and ethanol were mixed and ball milled for 24 hours with the weight ratio of 10:15:15:60. The obtained solution was slightly yellow and transparent, with the viscosity between 1000 - 8000 cp.

Step 2: preparation of YSZ tapes.
Powder of 8 mol % yttria stabilized zirconia (8YSZ) was mixed with the solvent of step 1 with the weight ratio of 60:40 and ball milled for 48 hours, forming a well-dispersed and viscous slurry. The slurry was then fed to a tape caster, forming tapes of thickness of ca. 200 μm.

Step 3: preparation of electrolyte.

The tape of 8YSZ was cut into small square pieces of 14 mm x14 mm and sintered at 1400 °C for 3 hours in air, forming dense and gas tight electrolyte with dimension of ca. 10 mm x10 mm.

Step 4: electrode preparation.
The IRE was made from a powder mixture of NiO (99 %, Sigma-Aldrich) and 8YSZ (TZ-8Y, Tosoh). Both powders contain a calcined part and a non-calcined part. Calcination of 8YSZ was performed at 1100 °C for 2 h and calcination of NiO was performed at 800 °C for 3 h. With the equal weight ratio, NiO, calcined NiO, 8YSZ, calcined 8YSZ and terpinol were mixed by planetary milling for 2 h, forming the IRE ink. The IRE ink was then screen printed on one side of the electrolyte of step 3. After sintering at 1350 °C for 2 hours, the powder mixture of 8YSZ and NiO is in good contact with the electrolyte and forms four IREs. The thickness of the sintered IREs was ca. 100 µm.

After sintering the IREs, the sensing electrode ink was screen printed on the opposite side of the 8YSZ electrolyte, forming four SEs such that each SE was preferably aligned to one IRE on the opposite side. The sensing electrode ink was made from $(La_{0.75}Sr_{0.25})_{0.95}MnO_{3\pm\delta}$ (LSM25), 8YSZ and terpinol, with the weight ratio of 40:40:20. The screen printed SEs was sintered at 1050 °C for 2 h.

The sintered IRE and SE was impregnated by nano-particles of 10 mol % Sm_2O_3 doped CeO_2, $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC). The impregnation was performed by dripping a nitrate solution onto the electrode surface and into the porous electrode followed by drying and decomposition of the dry nitrate at 700 °C for 2 h. The 1 M nitrate solution, $Ce_{0.8}Sm_{0.2}(NO_3)_x$, consisting of 20 mol % $Sm(NO_3)_3$ and 80 mol % $Ce(NO_3)_3$, was prepared from $Sm(NO_3)_3{\cdot}6H_2O$ (Alfa Aesar) and $Ce(NO_3)_3{\cdot}6H_2O$ (Alfa Aesar). Four times impregnation with the nitrate solution resulted in a SDC load of ca. 6 $mg{\cdot}cm^{-2}$ for the internal reference electrode and ca. 3 $mg{\cdot}cm^{-2}$ for the sensing electrode. The impregnated SDC particles were in a size of ca. 40 nano meters after the decomposition and covered completely the previously sintered particles including NiO, 8YSZ and LSM25.

Step 5: sensor preparation

After preparation of the IREs and SEs, Pt leads were adhered to the IREs by Pt paste, followed by a heat treatment at 700 °C for 1 h. In some embodiments the Pt leads may be replaced by thermocouples, e.g. the S-type thermocouples, such that the temperature of the IRE can be determined.

The glass seal was applied when IREs and SEs were ready and the Pt leads was adhered. Fine glass powder (< 200 mesh) with composition of SiO_2, 67.94 wt%, Al_2O_3, 14.91 wt%, Na_2O, 17.14 wt% was made into a paste with polyethylenglycol as the solvent, such that the ratio of glass powder to polyethylenglycol solvent is 80:20. The paste was then used to coat the IREs by brushing. To realize a hermetic seal, the glass paste covering the IREs was heated at 960°C for 2 h. The heating rate must be slow i.e. 1 °C·min^{-1} so that decomposition of the organics in the paste does not generate bubbles connecting to each other in the sintered glass seal.

After sealing, the final step of cell fabrication was to create a finely dispersed binary mixture of Ni/NiO, which was obtained by *in-situ* electrochemical reduction of part of the NiO. The electrochemical reduction was performed at an elevated temperature so that the cell resistance was decreased in some degree, and the electrochemical reduction of NiO could proceed smoothly. The typical reduction conditions were 664 °C, 1.0 V for 1 h and a power source like Gamry Reference 600 was used for the electrochemical reduction. The SEs were connected to the positive poles of the external power source such as Gamry Reference 600.

After reduction, the sensor with four pairs of IRE and SE was ready for use. The sensor was tested in air in the temperature range from 350 to 650 °C. Results of the test are shown in Fig. 11. “Pair 1, 2, 3 and 4” denotes each pair of electrically connected IRE and SE. “Theoretical” denotes the theoretical potential based on the gas composition the sensor was exposed to (i.e. air in the temperature range from 350 to 650 °C). Fig. 11 shows that the responses of the four electrode pairs agree to each other, and that the responses are very close to the theoretical value.

Switches to each of the four pairs of electrically connected IRE and SE, were included and realised using the Gamry Reference 600. The switches could be set to working mode (W), where the electrode pair was in operation mode and gas detecting, to idle mode (I), where the electrode pair was not in operation, and to recovery mode (R),

where the electrode pair was supplied with power such that the IRE could be recovered.

Example 2: Sensor with integrated heating element and temperature detector

A sensor comprising two IREs, two SEs, integrated heat element and temperature detector was prepared. The fabrication steps were:

Step 1: preparation of solvent.
PVP (Polyvinylpyrrolidone, K-15), PVB (polyvinyl butyral, B75H), PEG (Polyethylene glycol, PEG1000) and ethanol were mixed and ball milled for 24 hours with the weight ratio of 10:15:15:60. The obtained solution was slightly yellow and transparent, with the viscosity between 1000 - 8000 cp.

Step 2: preparation of YSZ tapes.
Powder of 5 mol % yttria stabilized zirconia (5YSZ) was mixed with the solvent of step 1 with the weight ratio of 60:40 and ball milled for 48 hours, forming a well-dispersed and viscous slurry. The slurry was then fed to a tape caster, forming tapes of thickness of ca. 200 μm.

Step 3: preparation of IRE ink and insulation layer ink.
The IRE was made from a powder mixture of NiO (99 %, Sigma-Aldrich) and 8YSZ (TZ-8Y, Tosoh) and SDC (American Elements). With the equal weight ratio, all solid powders and terpinol were mixed by planetary milling for 2 h, forming the IRE ink.

The insulation layer ink was made from alumina powder and terpinol. Alumina powder (42572, Alfa Aesar) was mixed with terpinol with the weight ratio of 80:20, and then ball milled for 2 hours, forming the insulation layer ink.

Step 4: screen printing
Four YSZ tapes prepared in step 2 were provided and screen-printed with different inks, e.g for heating element (e.g. a heater), temperature detector, IRE, conductive layer and insulation layer. The screen-printing of each ink was deposited in a specific pattern, e.g. circuits of a heater ink were deposited in a deliberately designed pattern on the 5YSZ tape prepared in step 2. Each screen-printing was followed by drying at

70 °C for 30 min. The inks of heaters (5571, ESL), temperature detectors (5559-B, ESL) and conductive layers (5570, ESL) were made of YSZ and platinum and were commercially available (commercial names in paranthesis). On one YSZ tape, several screen printings may be carried out in a specific order. For example, the heater and the temperature detector are preferred to be sandwiched between two layers of insulation layers to avoid electronic disturbance.

1) The first YSZ tape was used as the electrolyte. A conductive layer was screen printed on one side of the YSZ tape used as the electrolyte. After drying at 70 °C for 30 min, the IRE ink of step 3 was screen printed on the dried conductive layer, in a pattern such that two individual IREs were formed with complete or partial overlap with the conductive layer. After drying again, a conductive layer was screen printed on the opposite side of the YSZ tape, forming two connection pads for the sensing electrodes.

2) The second YSZ tape was used as a mechanical support of the temperature detector circuit. A layer of insulation layer ink prepared in step 3 was first screen printed on an YSZ substrate, followed by a drying at 70 °C for 30 min. Then a temperature detector circuit was screen printed on the insulation layer. When the temperature detector circuit was dry, another layer of insulation ink was printed over the temperature detector circuit, and dried.

3) The third YSZ tape was used as a support of the heater circuit. A layer of insulation layer ink prepared in step 3 was first screen printed on an YSZ substrate, followed by a drying at 70 °C for 30 min. Then a heater circuit was screen printed on the insulation layer. When the heater circuit was dry, another layer of insulation ink was printed over the heater circuit, and dried.

4) The fourth YSZ tape was used as a support of conductive layers, which is also denoted connection layers or connection pads. A layer of insulation layer ink prepared in step 3 was first screen printed on an YSZ substrate, followed by a drying at 70 °C for 30 min. Then a conductive layer was screen printed on the insulation layer in such a manner that six defined areas were formed, i.e. six connection pads were formed over the insulation layer. The six connection pads were used for electronic connection to the two IREs, the heater and the temperature detector.

Step 5: cross-layer electrical connection

Holes of diameter of ca. 1 mm were drilled at specified positions on the printed tapes of step 4. Platinum ink (5570 ESL) was fed by screen printing through these holes, forming conductive passages that were able to connect electrically the sensor circuits printed on different layers.

Step 6: lamination and sintering

The four YSZ tapes after step 5 were stacked in a specific sequence, followed by lamination in a warm isostatic presser at 85 °C for 3 minutes. The laminated stacks were then sintered at 1400 °C for 1h in air and become densified that also functions as sealing the IREs.

Step 7: lead connection

Pt leads were first adhered to the conductive layers of the heaters, the temperature detectors and the IREs by Pt paste at the external surface of the sensor, followed by a heat treatment at 700 °C for 1 h. The Pt leads may be optionally replaced by thermocouples, e.g. the S-type thermocouples, such that the temperature of the IRE can be determined.

The connection of Pt leads may be optionally followed by coating a layer of glass that provides additional mechanical strength to the Pt lead connection and/or additional gas tightness at the junctions where the Pt leads were in contact with the conductive layers of the IREs. To carrying out the glass coating, glass powder with the composition of SiO_2, 67.94 wt%, Al_2O_3, 14.91 wt%, Na_2O, 17.14 wt% was made into a paste with polyethylenglycol as the solvent. In the glass paste the weight ratio of glass powder to polyethylenglycol solvent was 80:20. The paste was then used to cover the junctions where Pt leads were in contact with the conductive layers by brushing. Coating of the glass paste was followed by a heat treatment at 960°C for 2 h.

Step 8: generating the binary mixture within the IREs

After Pt lead collection of step 7, IREs were then to be partially reduced by electrochemical method in order to form *in-situ* the finely-dispersed binary mixture of Ni/NiO. The typical reduction conditions are 664 °C, 1.2 V for 1 h and a power source like Gamry Reference 600 was used for the electrochemical reduction. During the electrochemical reduction, the conductive layers of SE were connected to the positive

poles of the external power source.

Step 9: preparation of the sensing electrodes.
After formation of the binary mixture of Ni/NiO, two SEs were prepared: one was sensitive to oxygen and the other was sensitive to nitrogen oxides (NO_x). Each SE was aligned to one IRE and was placed over one of the two connection pads. The oxygen sensitive electrode was made from the ink comprising $(La_{0.75}Sr_{0.25})_{0.95}MnO_{3\pm\delta}$ (LSM25), 8YSZ and terpinol, with the weight ratio of 40:40:20. The screen printed oxygen sensing electrode was sintered at 1050 °C for 2 h. After that the second SE sensitive to NO_x was prepared by screen printing the ink comprising $CaCO_3$, $Ba(NO_3)_2$ and terpinol, with the weight ratio of 5:70:25 on the location corresponding an IRE. After screen printing, the second SE was heated at 630 °C for 40 min. Then the sensor simultaneously responsive to oxygen and NOx was ready to use.

Items

The invention can be further described by the items listed below.

1. A sensor for gas sensing, comprising:
   - a solid electrolyte,
   - at least two sensing electrodes (SEs) in solid contact with the electrolyte, and
   - at least two internal reference electrodes (IREs) in solid contact with the electrolyte,
   wherein each IRE comprises a composite material, comprising a binary mixture of a metal and a metal oxide dispersed to form a three-dimensional network extending throughout the IRE,
   and wherein each SE is electrically connected with at least one IRE.

2. The sensor according to item 1, wherein each IRE comprises a further material or material mixture providing ion conductivity and electronic conductivity, and wherein the composite components and the further material are dispersed to form a three-dimensional network extending throughout the IRE.

3. The sensor according to any of the preceding items, wherein the sensor is potentiometric.

4. The sensor according to any of the preceding items, wherein the solid electrolyte is an oxide ion conductor.

5. The sensor according to any of the preceding items, wherein each of the IREs comprises different materials.

6. The sensor according to any of the preceding items, wherein all of the IREs comprise the same materials.

7. The sensor according to any of the preceding items, wherein the IREs are identical.

8. The sensor according to any of the preceding items, comprising three or more IREs, and wherein the IREs optionally comprise the same materials.

9. The sensor according any of the preceding items, wherein the binary mixture of the IRE is configured such the ratio of the components in the binary mixture can be recovered by electrochemical means.

10. The sensor according to any of the preceding items, further comprising electronic control means, preferably comprising a potentiostat, and one or more switches configured such that different operation modes of each IRE can be activated, such as working, idle, or recovery.

11. The sensor according to item 10, wherein the operation mode of each IRE is controlled independently of each other.

12. The sensor according to item 10, comprising at least three IREs configured such that at least one IRE is in working mode, at least one IRE is in idle mode, and at least one IRE is in recovery mode.

13. The sensor according to item 10, comprising at least four IREs configured such that at least two IREs are in working mode, at least one IRE is in idle mode, and at least one IRE is in recovery mode.

14. The sensor according to items 10-13, wherein the switches are contained in one electronic device.

15. The sensor according any of the preceding items, wherein each of the two or more SEs is electrically connected to a separate IRE.

16. The sensor according any of the preceding items, wherein each of the two or more SEs is electrically connected to two or more IREs.

17. The sensor according to any of the preceding items, wherein each of the two or more SEs is electrically connected to the same two or more IREs.

18. The sensor according to any of the preceding items, comprising SEs configured for detecting different gas types, thereby obtaining multi-gas functionality.

19. The sensor according to item 18, wherein the SEs are configured for detection of oxygen, and/or NOx, and/or COx, and/or SOx, and/or H_2S.

20. The sensor according to items 18-19, comprising at least two SEs for each gas type to be detected.

21. The sensor according to items 18-20, comprising at least three SEs for each gas type to be detected, and wherein each SE is electrically connected to a separate IRE, and wherein each IRE is configured to be operated in the three modes (working, idle or recovery), and wherein the operation mode of each IRE can be configured to be controlled independently or dependently of each other.

22. The sensor according to any of the preceding items, comprising an integrated heating source and a temperature control system, or parts of a temperature control system.

23. The sensor according to any of the preceding items, further comprising a substrate, or support layer.

24. The sensor according to item 22, wherein the heating source is embedded into the substrate or support layer, or partially or completely covered by one or more insulating layer(s).

25. The sensor according to items 22 and 24, wherein a temperature detector is embedded into the substrate or support layer, or partially or completely covered by one or more insulating layer(s).

26. The sensor according to any of the preceding items, wherein the contact area between each IRE and the solid electrolyte is below 9 mm^2, more preferably below 7 mm^2, and most preferably below 5 mm^2.

27. The sensor according to any of the preceding items, further comprising two or more electrolytes.

28. The sensor according to any of the preceding items, wherein the IREs and SEs are disposed on opposite surfaces of the electrolyte.

29. The sensor according to any of the preceding items, wherein the IREs and SEs are disposed on the same surface of the electrolyte.

30. Method of fabricating a sensor, said method comprising the steps of:
- providing at least one electrolyte layer, at least two IREs, and one or more SE(s), wherein the SE(s) and IREs are in solid contact with the electrolyte, and wherein the electrolyte separates the SE from the IRE,
- providing a power source, one or more switch(es), and
- connecting the power source and switch(es) to the IREs such that the IREs can be operated in three modes (working, idle, and recovery), and configured such that the operation of multiple IRE(s) can be controlled independently or dependently of each other.

31. Method of assembling a sensor with IRE(s) with an integrated heating source and a temperature control system, said method comprising:
- providing one or more electrolyte(s),
- depositing onto the electrolyte(s) by screen-printing one or more ink(s) of an IRE, a heating element, a temperature detector, a conductive layer, and insulation, wherein the order of the inks and the deposited pattern of the inks are configured to a defined design, and
- optionally laminating and co-sintering multiple screen-printed electrolytes.

32. Use of the sensor according to items 1-30 for detection of oxygen, and/or NOx, and/or COx, and/or SOx, and/or H_2S.

Claims

1. A sensor for gas sensing, comprising:
   - a solid electrolyte,
   - at least two sensing electrodes (SEs) in solid contact with the electrolyte, and
   - at least two internal reference electrodes (IREs) in solid contact with the electrolyte,
   wherein each IRE comprises a composite material, comprising a binary mixture of a metal and a metal oxide dispersed to form a three-dimensional network extending throughout the IRE,
   and wherein each SE is electrically connected with at least one IRE.

2. The sensor according to claim 1, wherein each IRE comprises a further material or material mixture providing ion conductivity and electronic conductivity, and wherein the binary mixture of a metal, a metal oxide and the further material are dispersed to form a three-dimensional network extending throughout the IRE.

3. The sensor according to any of the preceding claims, wherein each of the IREs comprises different materials.

4. The sensor according to any of the preceding claims, wherein all of the IREs comprise the same materials, or wherein the IREs are identical.

5. The sensor according any of the preceding claims, wherein the binary mixture of the IRE is configured such the ratio of the components in the binary mixture can be recovered by electrochemical means.

6. The sensor according to any of the preceding claims, further comprising electronic control means, preferably comprising a potentiostat and one or more switches configured such that different operation modes of each IRE can be activated, such as working, idle, or recovery.

7. The sensor according to claim 6, wherein the operation mode of each IRE is controlled independently of each other.

8. The sensor according to any of claims 6-7, comprising at least three IREs configured such that at least one IRE is in working mode, at least one IRE is in idle mode, and at least one IRE is in recovery mode, or comprising at least four IREs configured such that at least two IREs are in working mode, at least one IRE is in idle mode, and at least one IRE is in recovery mode.

9. The sensor according any of the preceding claims, wherein each of the two or more SEs is electrically connected to a separate IRE, or connected to two or more IREs, or connected to the same two or more IREs.

10. The sensor according to any of the preceding claims, comprising SEs configured for detecting different gas types, thereby obtaining multi-gas functionality.

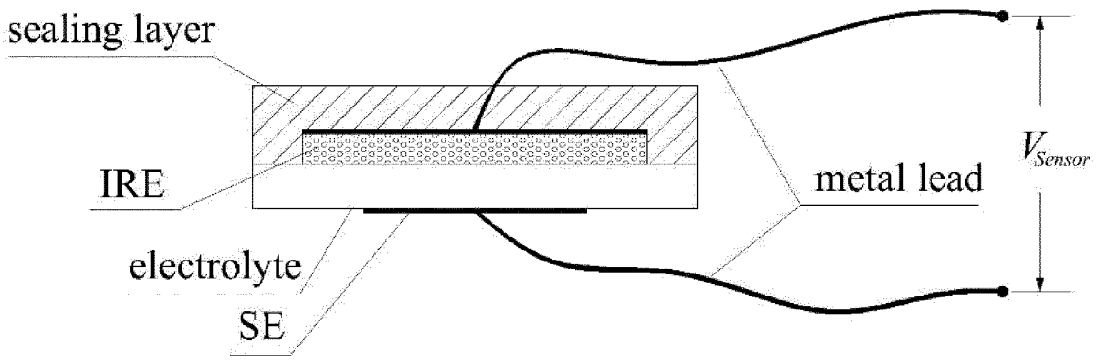
11. The sensor according to claim 10, wherein the SEs are configured for detection of oxygen, and/or NOx, and/or COx, and/or SOx, and/or H_2S.

12. The sensor according to any of claims 10-11, comprising at least two SEs for each gas type to be detected.

13. The sensor according to any of the preceding claims, further comprising a substrate, or support layer.

14. The sensor according to any of the preceding claims, comprising an integrated heating source and a temperature control system or parts of a temperature control system, wherein the heating source and/or the parts of the temperature control system optionally are embedded into a substrate or partially or completely covered by one or more insulating layer(s).

15. The sensor according to claim 14, further comprising an integrated temperature detector, wherein the temperature detector optionally is partially or completely covered by one or more insulating layer(s).



IRE: internal reference electrode
SE: sensing electrode
V_{Sensor}: voltage between IRE/SE, a measure of pO_2

Fig. 1

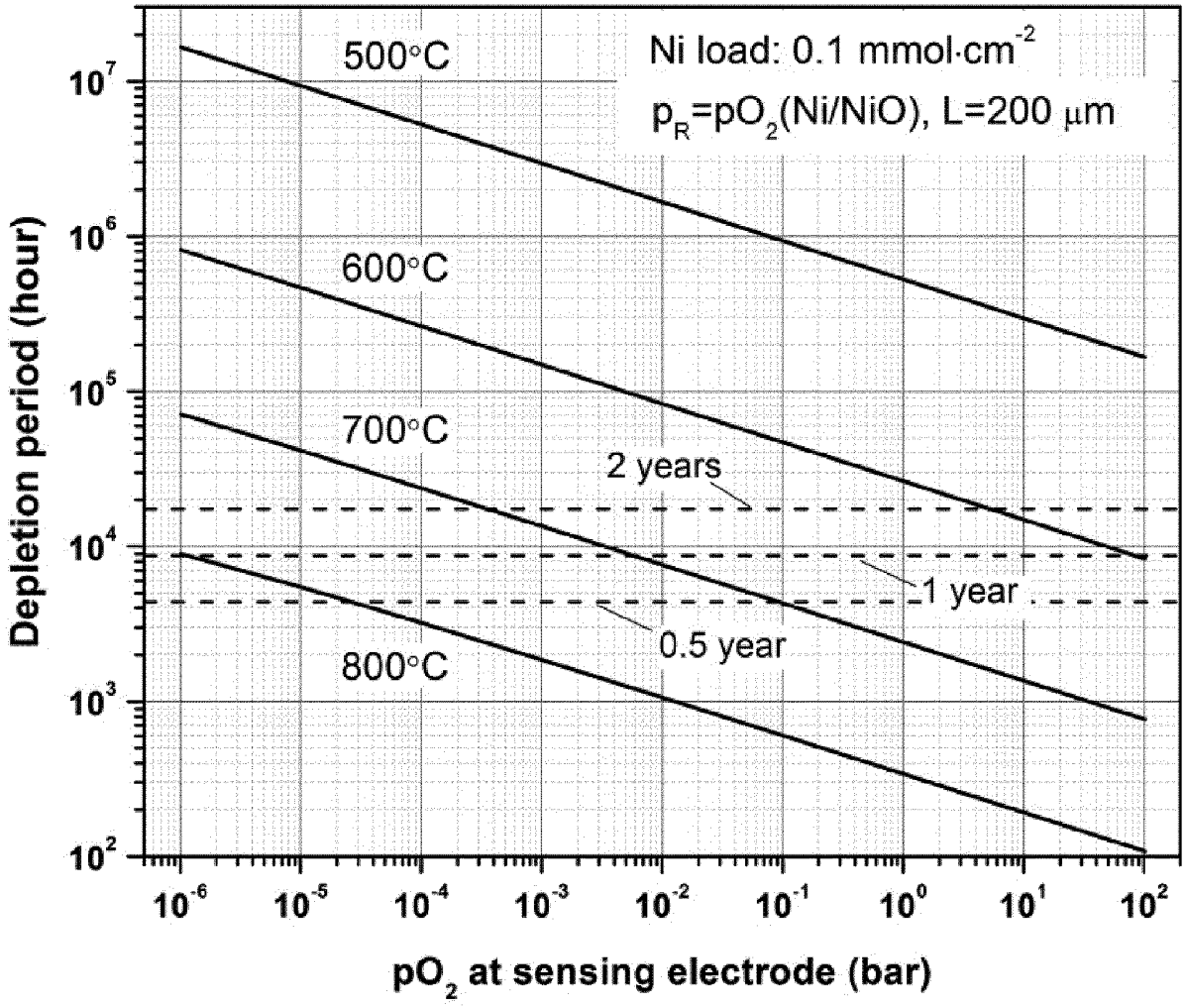

500°C
Ni load: 0.1 mmol·cm-2
pR=pO2(Ni/NiO), L=200 μm
600°C
700°C
2 years
1 year
0.5 year
800°C
Depletion period (hour)
pO2 at sensing electrode (bar)

Fig. 2

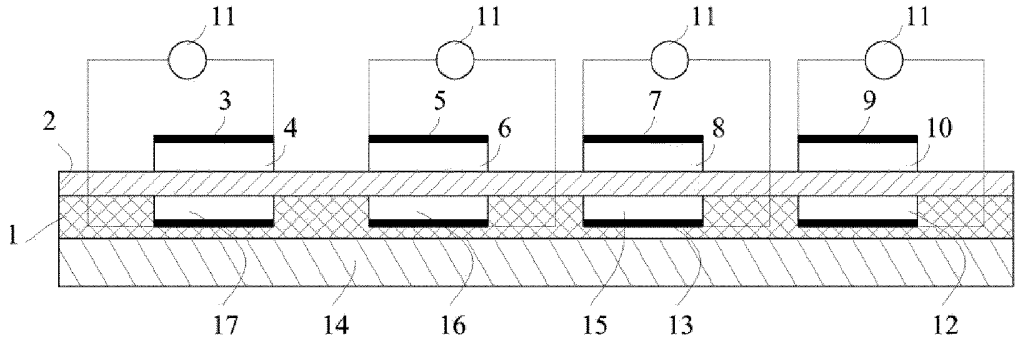

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Fig. 3

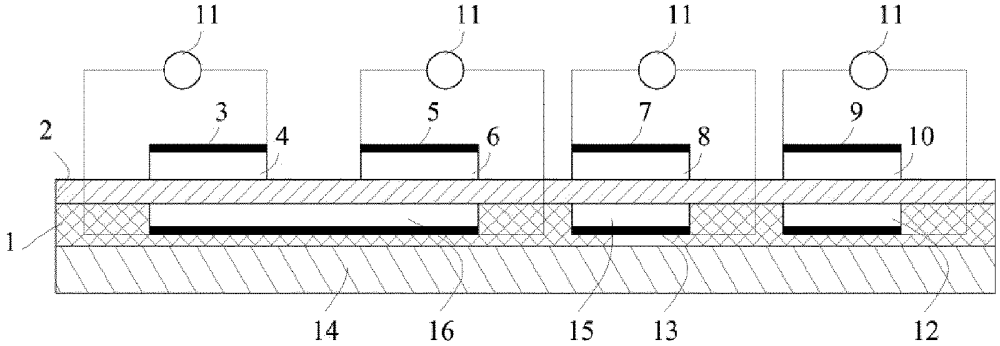
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Fig. 4

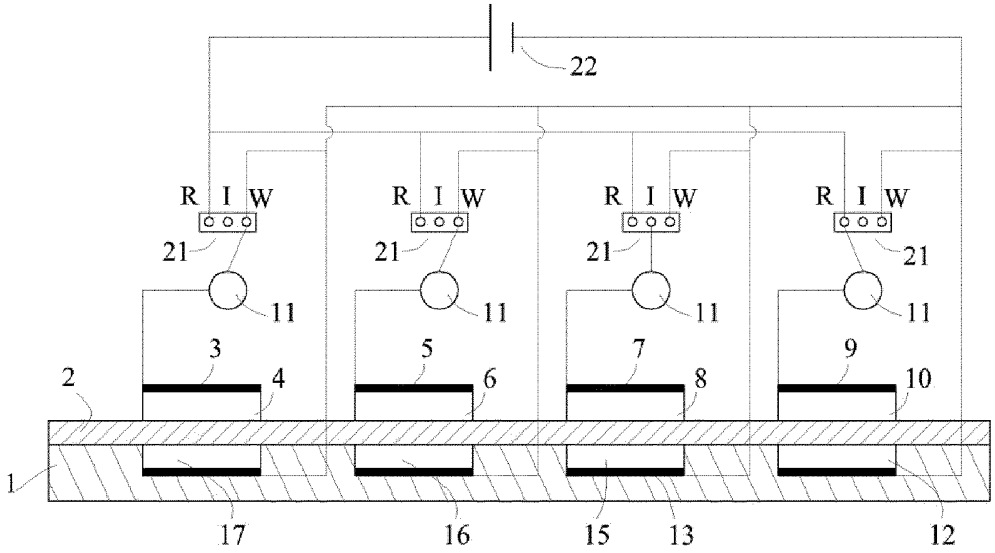
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Fig. 5

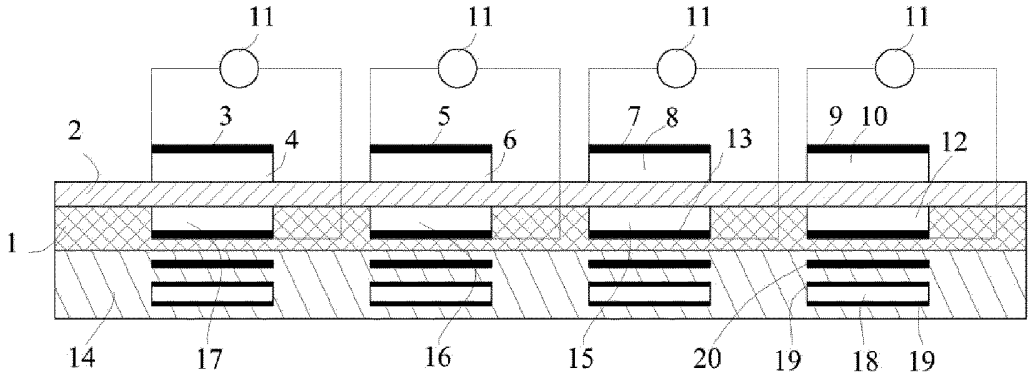
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Fig. 6

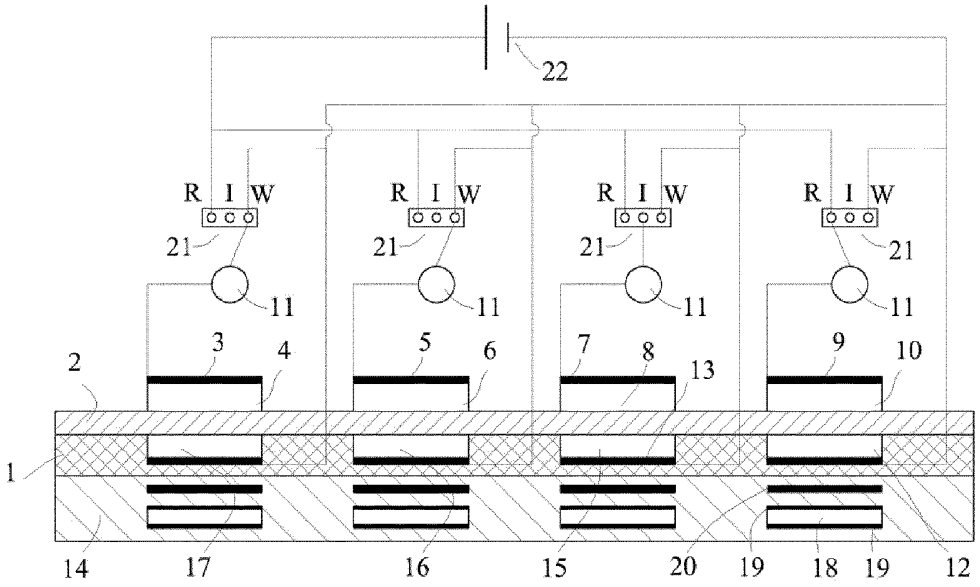
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Fig. 7

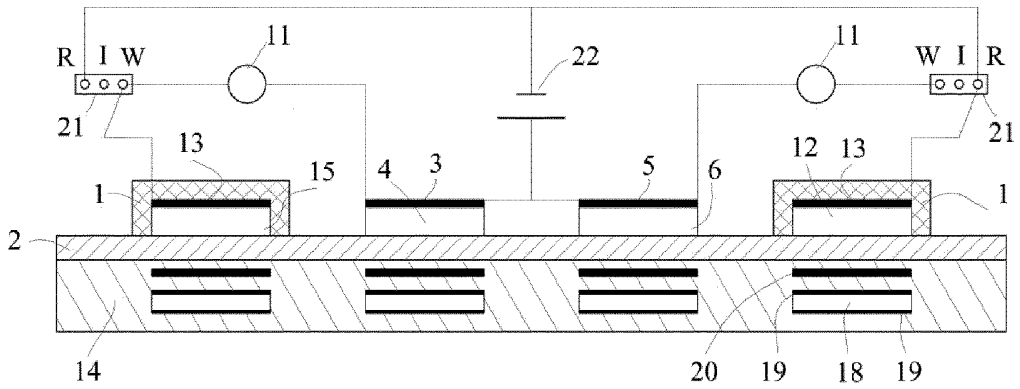
R I W
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Fig. 8

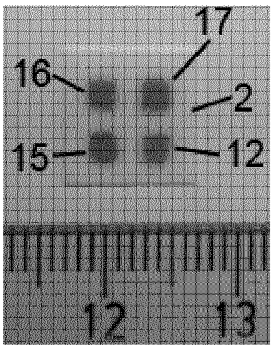
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Fig. 9

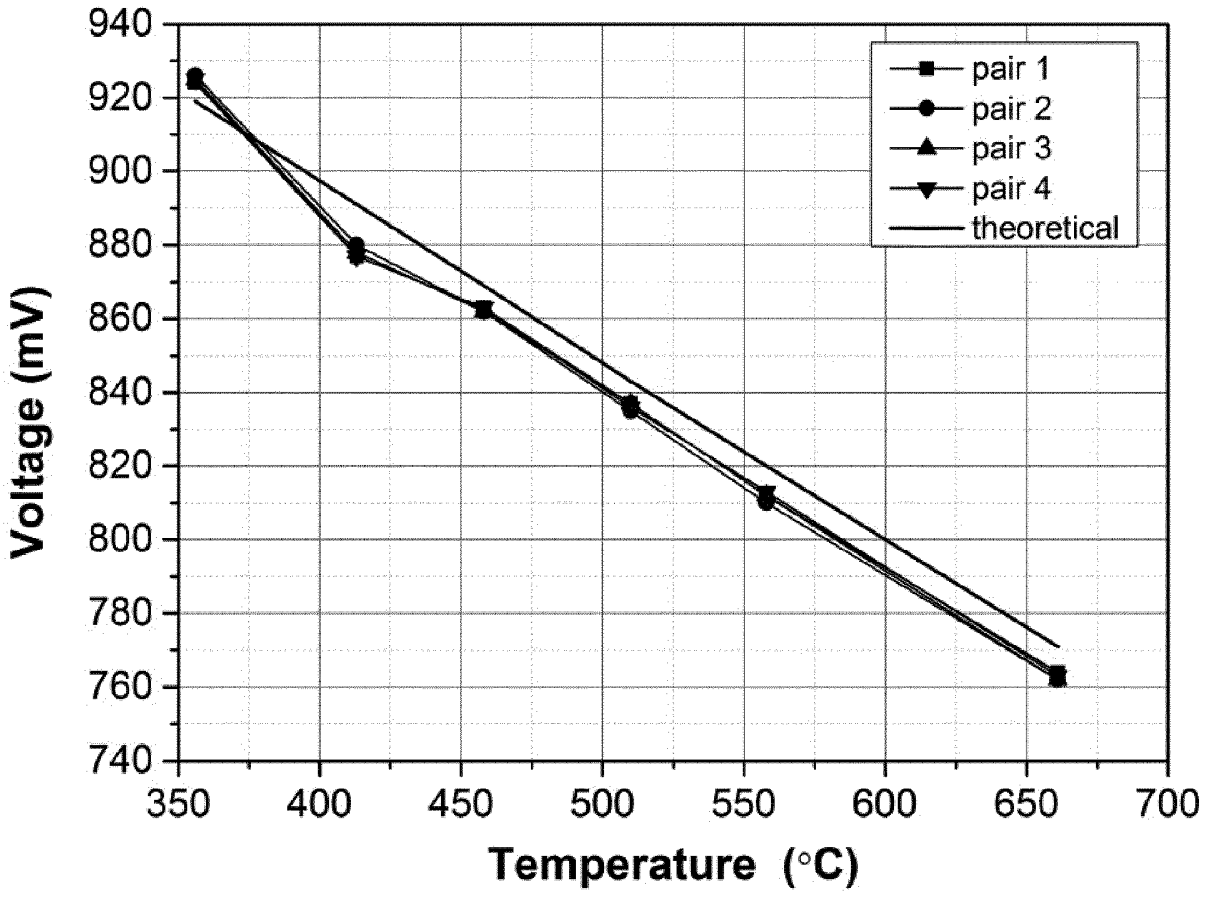
940
920
900
880
860
840
820
800
780
760
740
350
400
450
500
550
600
650
700
Voltage (mV)
Temperature (°C)
pair 1
pair 2
pair 3
pair 4
theoretical

Fig. 10

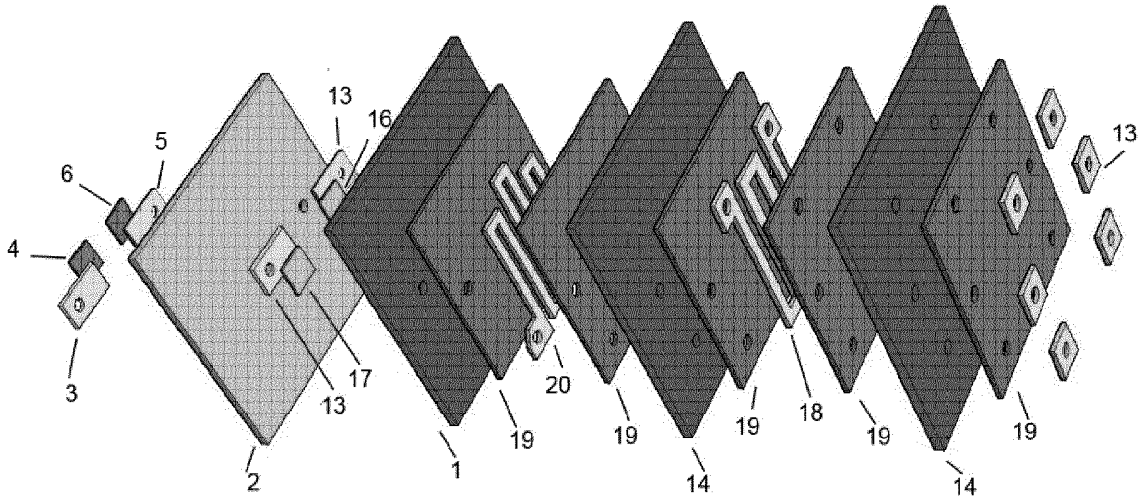

Fig. 11

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/058065

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N27/27 G01N27/407 G01N33/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2013/160271 A1 (UNIV DENMARK TECH DTU [DK]) 31 October 2013 (2013-10-31) cited in the application the whole document	1-15
Y	WO 95/30146 A1 (COPCUTT ROBERT C [GB]; MASKELL WILLIAM C [GB]) 9 November 1995 (1995-11-09) page 5, line 6 - line 31; figure 5	1-15
A	US 5 954 930 A (NAEFE HELFRIED [DE] ET AL) 21 September 1999 (1999-09-21) column 5, line 52 - column 6, line 42; figure 5	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 June 2016	14/07/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Purdie, Douglas

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/058065

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		WO 9522050 A1	17-08-1995